

Patterning of Flexible Organic Light Emitting Diode (FOLED) stack using an ultrafast laser

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Abstract: A femtosecond laser has been successfully utilized for patterning thin Flexible Organic Light Emitting Diode (FOLED) structures of individual layer thickness around 100nm. The authors report in this paper a step-like ablation behavior at the layer interfaces which accounts for a local removal of entire layers. Various surface analyzing techniques are used to investigate the morphologies and chemical compositions within and in the vicinity of the ablation areas. This study opens a new avenue in selectively ablating different layers from a multilayer stack on flexible substrates using fs lasers allowing post deposition structuring of large area flexible organic electronic devices.

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1. Introduction

Since the first organic light emitting diode (OLED) device is invented at Eastman Kodak by C. Tang and S. Van Slyke in the 1980s [1], there has been a lot of research on the fabrication of flexible and reliable OLED devices [2,3]. Organic flexible electronic devices have many advantages over conventional non bendable organic electronic devices. These devices are thin, clear (transparent) and light weight. Flexible OLEDs have lot of potential in applications such as the displays, mobile phones, television, and lighting. Screen printing and Ink jetting are the extensively investigated techniques for patterned deposition of OLED devices [4–7]. The main constrain of these techniques are the achievable minimal feature sizes along with maintaining the thickness homogeneity within the individual layers. On the other hand large area homogeneity can be extremely well controlled using unpatterned deposition techniques such as spin coating. One of the major applications of the laser patterning is in the roll to roll processing of OLEDs [8]. Post deposition laser processing is an alternative to patterning techniques like gravure printing, slot-die coating and photolithography and can preserve the much better layer homogeneities achieved by continuous large area coating. By such laser ablation patterning very fine feature sizes can be obtained with high process speeds from homogeneously deposited layer sequences. Proper power density adjustment, wavelength and pulse width selection of the laser beam has to be effectively utilized for selective removal of different thin layers which is crucial for the roll to roll processes for flexible electronics [9–11].

When a multilayer material like a flexible OLED stack, which has got different optical absorption across the stack, is ablated using ns laser pulses, selective ablation of individual layers becomes difficult [12]. Moreover, laser pulses will also lead to the thermal loading on the material. Ablation of the OLED material stack using ultrafast pulses is less dependent on wavelength and absorption spectra due to the nonlinear effects generated in the material and does not induce thermal loading on the material [13,14]. J. Kruger et al. give a detailed explanation of the ultra short pulse interaction with polymers [14]. D. Karnakis et.al. has used picosecond lasers to ablate thin film layers and have explained the picosecond ablation phenomena [15]. They utilize two different wavelengths for ablating two different layers on a device stack. This is due to the influence of optical absorption properties of those layers. In this paper a femtosecond laser operating at 800 nm (150 fs) is used to ablate a multilayer stack of various optical absorption coefficients which clearly shows an ablation process which is less dependent on the optical absorption characteristics.

2. OLED device structure

If an organic emissive layer, LEP (Light Emitting Polymer), is sandwiched between an anode and a cathode layer, an OLED is formed. The LEP, a conjugated polymer emits light when a potential is applied between anode and the cathode layers. The potential difference created between the anode and the cathode leads to the flow of electrons from cathode to anode. This flow will make the emissive layer rich in negative charge causing electron hole recombination in the organic layer thereby emitting light. When these layers are deposited on PEN (Polyethylene Naphthalate) or PET substrates, they form a flexible OLED. A detailed structure of a flexible OLED device is as given in the Fig. 1. The substrate, either PEN or PET, gives mechanical stability to the OLED stack. The barrier acts against moisture leakage, preventing damage of the OLED device. The barrier layer is made out of SiN (Silicon Nitride) top layer and a special type of polymer. The transparent conductor, ITO (Indium Tin Oxide) acts as an anode and plays a vital role in the distribution of charged carriers to the stack.

On top of the ITO anode, the PEDOT: PSS (conducting polymer) hole injection layer is deposited by spin coating from an aqueous solution. The active LEP is then spin coated on the PEDOT: PSS layer which in turn is covered by a low work function barium or calcium cathode layer capped with Aluminum. Another barrier layer is applied on top of the whole

stack to form a complete OLED stack. In order to provide electrical connection to the anode and cathode layers laser ablations of different layers in the OLED stack can be carried out and later filled with conductive ink or paste. The refractive index of these layers at 800 nm is found to be 1.63, 1.86, 1.67 and 1.31 for ITO, SiN, LEP and PEDOT respectively.

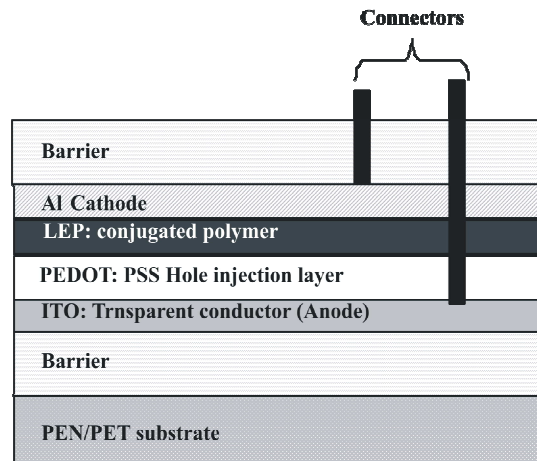


Fig. 1. Detailed structure of OLED showing different layers

3. Experiment

In our experiments a Ti:Sap 800 nm, 150 fs, 1 KHz laser system is used for patterning the stack with a beam focused on multilayer to a spot size of around 18 μm . Typical experimental setup is as shown in the Fig. 2. Specific layer sequences and thicknesses are chosen which represent a functional OLED structure. At first a barrier layer is deposited on flexible PEN substrates over which a 130nm ITO (Indium Tin Oxide) is sputtered. On this stack a 100nm PEDOT (organic hole injection polymer) and a 80nm LEP (Light Emitting Polymer) layer is spin coated to form the whole stack. The final stack has a layer sequence as represented in the inset of Fig. 2.

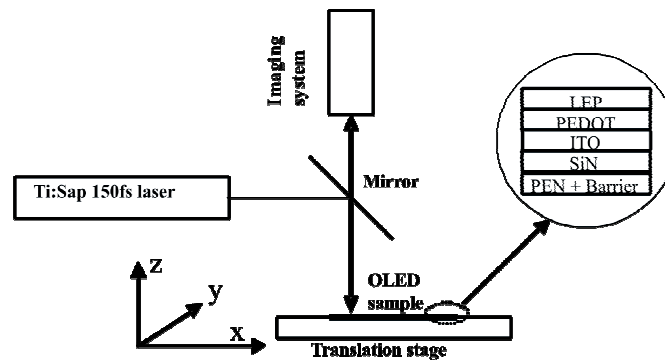


Fig. 2. Schematic of the experimental setup for single shot, multiple shot and patterning experiments on the OLED stack. Inset shows the layer sequence used for the experiments.

The OLED stack is positioned on a motorized computer controlled two axis translation stage which is utilized for single shot and patterning experiments. The main task is to effectively ablate through the LEP and PEDOT organic layers and stop on ITO and/or on barrier layers without damaging those layers. By changing the speed of the stage, laser pulse overlap can be tuned either for single shot or for patterning.

4. Results and discussion

For studying the ablation behavior through the OLED stack, single shot ablation experiments are performed first. The experiments are carried at various laser fluences from 0.07 J/cm² to 1.6 J/cm². Stylus profilometry is used to carry out the depth measurements of the ablated region. Figure 3 shows the graph of ablated depth achieved at various fluence levels. The graph also clearly shows that there is a very large process window from 1 shot per location to 4 shots per location which is very important if patterning is need. It can also be seen that the depth stay almost a constant till 4 shots per location at a particular laser fluence.

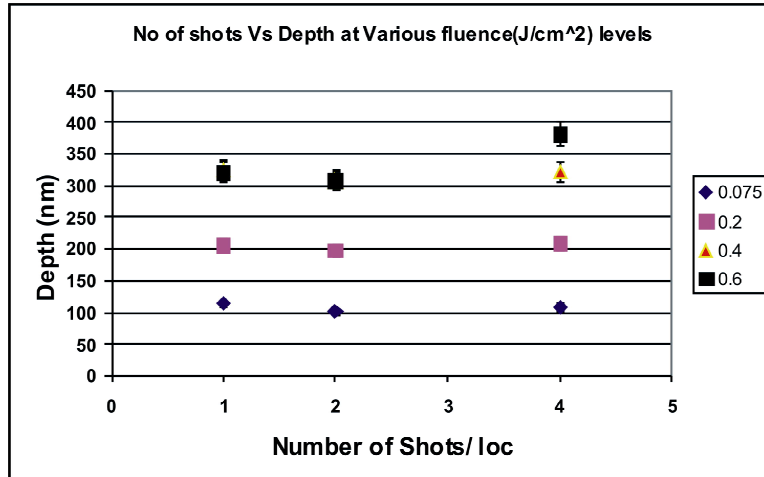


Fig. 3. Various depths achieved at various laser fluence levels. There exists a process window of at least 4 shots per location for the patterning.

Typical measurement results are shown in Fig. 4(a)–4(c). At fluence of 0.075 J/cm² a depth of 84 nm is obtained at the central position of the ablation area which indicates that the top LEP layer is completely removed and PEDOT is exposed but almost unaffected. This indicates a selective removal of the LEP layer. Furthermore, a depth of 199 nm is obtained in the flat central bottom of the ablation crater from the measurements at 0.20 J/cm². It indicates that the LEP and the PEDOT layers are completely removed in this case and ITO is exposed and almost unaffected (for comparisons see also the stack sequence sketched in Figs. 1, 2 and 5). When the laser fluence is increased to 0.60 J/cm² similar measurements reveal a depth of 324 nm in the central flat bottom region.

It seems that LEP, PEDOT and the ITO layers (nominally 80 nm + 100 nm + 130 nm) are completely removed leaving the barrier exposed but almost untouched. Microscopic images of the corresponding ablated regions are shown in the inset of the Fig. 4(a)–4(c). From a comparison of the ablation craters in the deposited layer stacks as observed through an optical microscope and in the depth profilometer measurements, it can be seen that there is indeed a color change for the different exposed layers confirming the complete and controlled removal of the upper layers. The same ablation craters are also measured by a white light optical profiler (WYKO) for each and plotted together with the profilometer values in Fig. 5. Similar depths are measured using the two techniques on the ablated stack again confirming that the depths obtained are in unison with the nominal thickness of specific layers deposited on the substrate.

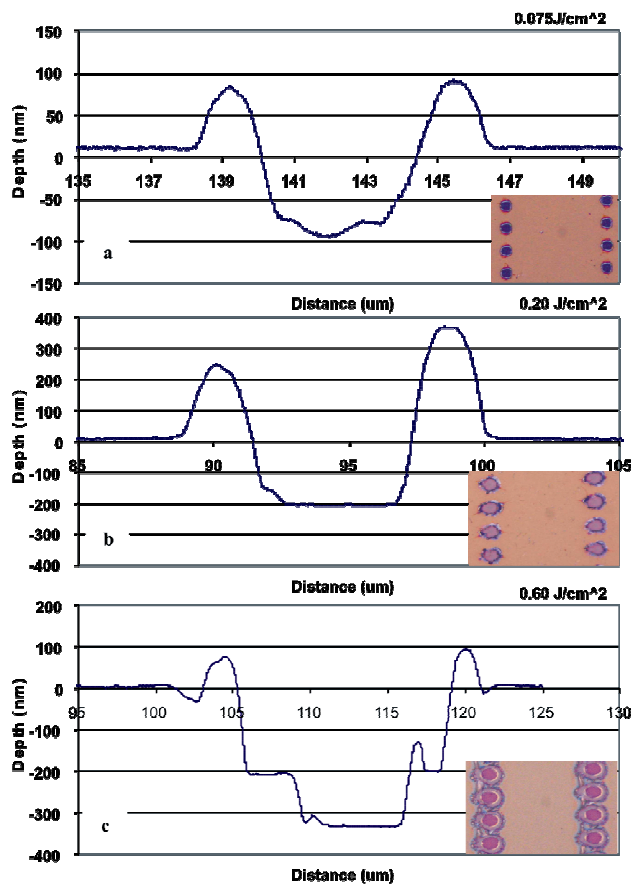


Fig. 4. Dektak profilometry showing the depth of the patterned layers. The inset pictures are the respective microscopic images (a) Stopping on PEDOT (LEP removed) (b) Stopping on ITO (LEP and PEDOT removed) (c) Stopping on barrier (LEP, PEDOT and ITO removed)

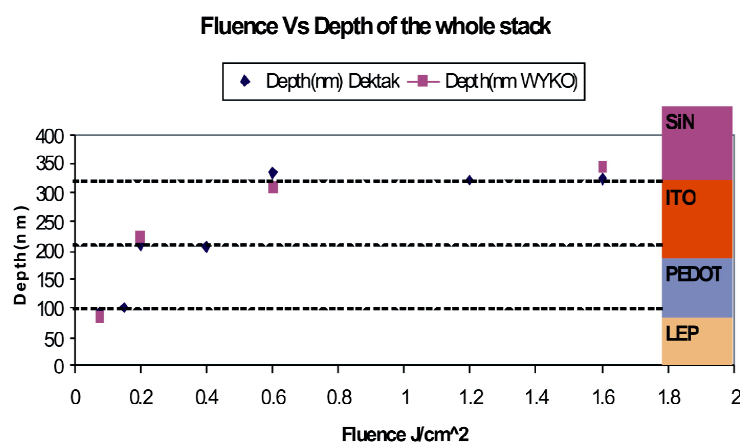


Fig. 5. Ablation depth values from profilometry measurements (squares) and from white light interferometry (Diamond) compared with layer thicknesses of the flexible OLED stack

As mentioned before, the femtosecond ablation is a complex phenomenon [14] and the selective ablation of the layers accounts as a result of various nonlinear processes generated during laser material interaction. It can be observed that the optical absorption of the material does not play a dominant role in the ablation of various layers. This can be explained by comparing the spectra shown in the Fig. 6 and the wavelength (800 nm) used for ablation. Considering (an example) the layer stack sequence in the inset of Fig. 2 it is evident that LEP would get less linear absorption than PEDOT at 800 nm. This means that if there is an optical absorption dependency, it would be impossible to achieve a clean ablation of LEP on PEDOT since PEDOT layer will be affected earlier than LEP layer in the ablation process.

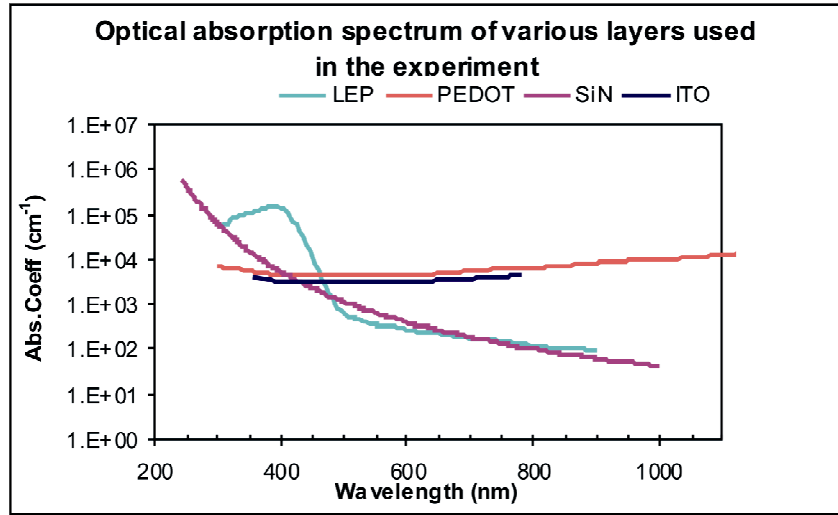


Fig. 6. Optical absorption spectrum of various layers used

A more detailed examination of the graph in Fig. 5 reveals a step like behavior. The laser pulse seems to attack the uppermost layer only above a certain fluence threshold but then as a removal of the entire layer after which the subsequent layer is exposed to the surface. Partial removal of a layer is not observed in all these experiments. In other words, the ablation seems to remove the different layers almost digitally, either no ablation or complete removal. For better illustration the interface positions are therefore represented as dotted lines in the graph. This step like behavior cannot be explained by different multiphoton absorption probabilities for each layer material in the stack, influencing the ablation behavior [14]. The latter would rather explain an ablation with different efficiencies for each layer but not the observed influence of the interfaces. It is known that surface acoustic waves and stress confinement are generated from ultrashort laser pulse interaction with the material [16–18]. This can potentially cause spallation of complete layers starting with delamination at the interfaces and thereby a step-like ablation behavior. This would also give an explanation for the stepped edges of the ablation craters but more investigations are needed to fully understand this phenomenon.

In order to have a better understanding of the chemical composition of the laser ablated region SEM/EDAX (Scanning Electron Microscopy and Energy Dispersive Spectroscopy) measurements are carried out. The important question to be answered is whether the laser process has actually removed specific layers and whether there is any residue in that region. The EDAX measurements are performed at the centre of the ablated regions with an acceleration voltage of 10 kV with a spot size of 4 μm and penetration depth would be typically around 1 μm for the stack and therefore the EDAX spectrum reflects information from all remaining layers. These measurements are first done on the single pulse ablated samples.

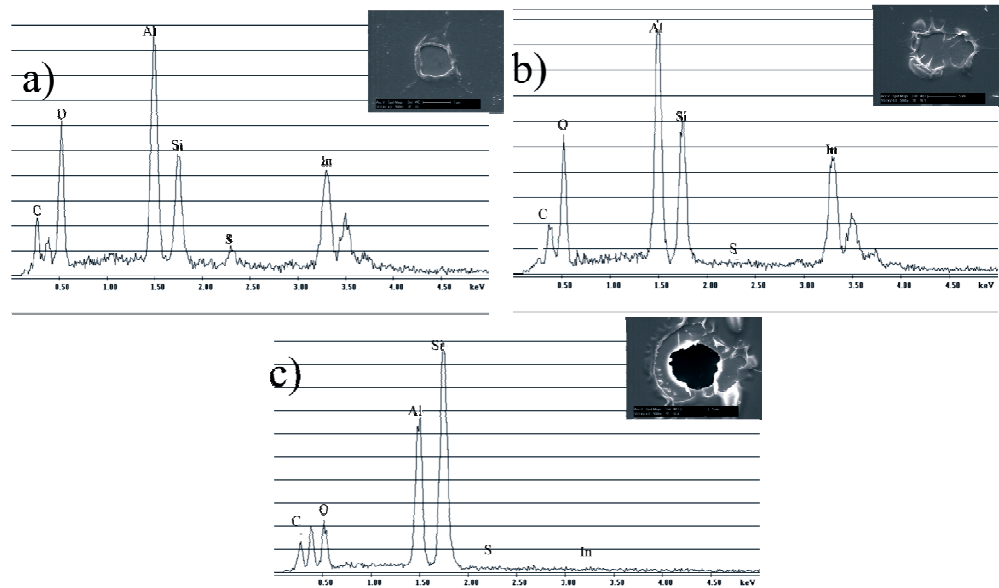


Fig. 7. The SEM image (inset) and the EDAX spectra of the various laser ablated regions within the OLED stack (a) PEDOT is exposed; 'S' peak visible (fluence: 0.075 J/cm²) (b) ITO is exposed; 'S' peak disappears and 'In' peak is still visible (fluence: 0.20 J/cm²) (c) SiN is exposed; both 'S' and 'In' peaks disappear and 'Si' peak still visible (fluence: 0.60 J/cm²)

Figure 7(a), shows the SEM image and the EDAX spectra of the ablated region at a laser fluence of 0.075 J/cm² (LEP layer removed). The Sulphur (S) peak confirms the presence of PEDOT layer. Similarly the Fig. 7(b) shows the SEM micrograph and EDAX spectrum of a sample that received a laser fluence of 0.20 J/cm². Here, the absence of Sulphur peak indicates the selective removal of both, the LEP and the PEDOT layer and the presence of Indium (In) implies that the ITO layer is still present. In the EDAX spectrum of Fig. 7(c) both 'S' and 'In' peaks no longer appear but the Silicon (Si) peak appears even stronger. From this and from the depth profile results we can clearly conclude that both PEDOT and ITO layers are removed and ablation is effectively stopped on the SiN layer which is a part of the barrier layer (see Fig. 5). The predominant Aluminum (Al) peaks in all the EDAX spectra are due to an 80 nm thick film of the same deposited for the white light Interferometry (WYKO) measurements to enhance the reflectivity. Figure 7 (the SEM micrographs, see the inset) also confirms the hypothesis that complete (spallation) removal of entire layers happens. Similar measurements are carried out on samples patterned with overlapping to verify whether it is indeed possible to create larger patterns in the LEP and PEDOT layers without affecting the ITO layer below.

Figure 8(a)–8(c) shows the WYKO, Dektak and microscopic images of a patterned line which is made by selectively ablating LEP and PEDOT layers and effectively stopping on an ITO layer. It is observed that there is no thermal damage on the sample. This is due to the fact that the ultrashort pulse duration is less than that of the time needed to achieve thermal equilibrium for most of the materials, which are in the picosecond regime. EDAX measurements are also carried out to confirm whether the ITO layer is intact. The result is shown in Fig. 9. The effective fluence achieved by spatially overlapping pulses is 0.19 J/cm² which confirms the selective line-patterning of the above said layers without removing the ITO. The absence of Sulphur peak in the EDAX spectrum again confirms that the PEDOT layer is selectively patterned and ITO remains. The appearance of the 'In' peak and the rest of the spectrum are comparable to the situation seen in Fig. 7(b) even though the effective fluence is not applied in a single pulse.

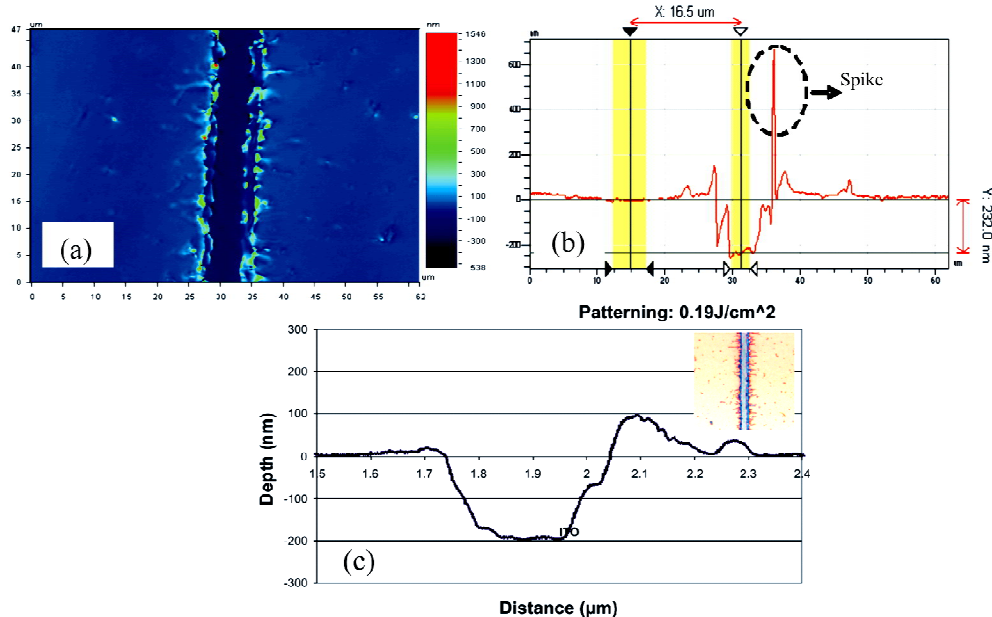


Fig. 8. (a) White light interferometer image of a patterned line (b) depth measurement obtained from the interferometer. The spike shown in the figure is due to the large flakes formed by the delamination of the layer during laser ablation. This can also be seen in the figure (a) at the ablation edges (c) Dektak measurement and the microscopic image of the patterned line.

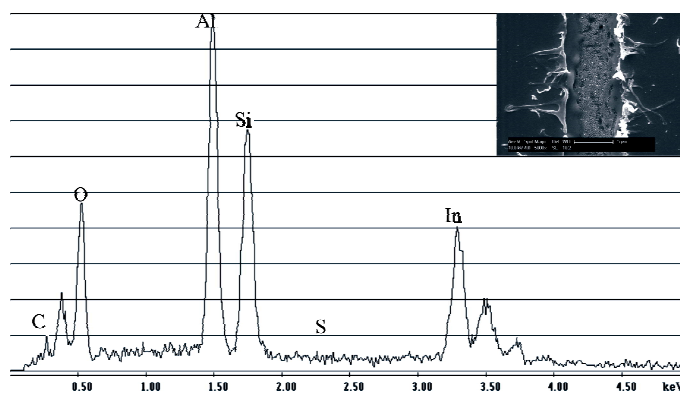


Fig. 9. The SEM image (inset) and the EDAX spectrum of laser scribed line showing that the LEP and PEDOT layers are completely removed at an effective fluence of 0.19 J/cm². The presence of 'In' peak confirms the presence of ITO layer

5. Conclusion

In conclusion the selective laser ablation of thin organic layers of OLEDs deposited on flexible substrate is achieved using an ultrafast (fs) laser. Systematic analysis of the results shows that the selective ablation and patterning is possible without affecting the underlying layers. A step like ablation phenomenon is observed at the layer interfaces which facilitate the removal of entire layers without affecting underneath structures. The results show that there is no significant affect of optical absorption in the ablation behavior of the layers. This phenomenon offers a new very advantageous approach for laser patterning of flexible OLED stacks or other materials consisting of very thin functional multilayers. Shock wave creation

and stress confinement in the irradiated areas could potentially explain the observed effects but further studies will be needed to fully understand these effects.

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